

## Effect of Acrylate Copolymers on the Rheological Properties of Cement Pastes, Part II

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**Abstract:** Three composition ratios of poly[acrylic acid (AA)-co-butylmethacrylate (BuMA)] Na were prepared in alcohol solution using azo-bis-isobutyro-nitrile as initiator (ABIN). The water-soluble copolymers were characterized by FT-IR, <sup>1</sup>H NMR, mass spectra, DSC and viscosity. The effect of water-soluble copolymers on the rheological properties of Ordinary Portland Cement (OPC) pastes was investigated. The results showed that the addition of aqueous solutions from the prepared copolymers to the cement improve most of the specific characteristics of OPC. As the dosage of water-soluble copolymer increased, the water demand decreased, whereas the setting times (initial & final) were prolonged. The combined water content and compressive strength of the hardened cement pastes were increased while the total porosity decreased at all ages of hydration.

**Key words:** Water-soluble copolymer • Ordinary Portland cement • Water consistency • Setting time  
• Combined water • Porosity • Compressive strength

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### INTRODUCTION

Chemical admixtures are polymers widely used as water reducing admixtures in concrete [1-3]. They increase the workability of the mixture enabling the lower water/cement (W/C) ratio to be used. Lower W/C ratios lead to higher compressive strength and improved durability [4]. Polymers that are being used with cement are polymer dispersions, redispersible polymer powders, water-soluble polymers, liquid resins and monomers [5, 6]. Generally, in cement based materials containing polymer, the polymer is added as an aqueous dispersions (latices). Compatible styrene butadiene emulsions, acrylate or vinyl acetate emulsions can develop small polymer domains or thin films between cement particles and even at fibre-matrix interfaces [6-8]. The main role played by these compounds is related to the surface-active constituents present in the polymer. The long-chain sulphonated compounds, hydroxy carboxyl acid groups etc. promote the surface-active properties of the admixtures. These properties vary with the molecular size of the compound. The effectiveness of the admixture depends on various

factors such as the chemical nature and molecular weight of the polymer, particle size distribution and composition of the binder, dosage of admixture and temperature. It is, therefore, important to have a methodology for selecting the appropriate admixture for the given cement and application [4, 7, 9-11].

The present work aims to study the preparation and characterization of poly [AA-co-BuMA]Na via FT-IR, <sup>1</sup>H NMR, mass spectra, DSC and viscosity. The purpose of this study is to investigate the effects of the prepared copolymer on the physico-mechanical properties of the cement pastes and to obtain basic data necessary to develop appropriate polymer for cement modifier.

### MATERIALS AND METHODS

**Synthesis and characterization of water-soluble copolymers:** Water-soluble copolymer (acrylic acid-butylmethacrylate) or poly[AA-co-BuMA] with various ratios of hydrophilic chains (M<sub>1</sub> = 99: 01, M<sub>2</sub> = 97: 03, M<sub>3</sub> = 95: 05 wt.%) were prepared by solution polymerization using azo-bis-isobutyro-nitrile (ABIN) as an initiator and

Table 1: The chemical composition of the raw materials, mass%

| Oxides Materials | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MgO  | SO <sub>3</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | L.O.I |
|------------------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|-------------------|------------------|-------|
| PCC              | 21.48            | 6.03                           | 4.22                           | 64.29 | 0.68 | 0.39            | 0.21              | 0.11             | 1.32  |
| G                | 0.58             | 0.14                           | 0.11                           | 30.08 | 0.13 | 45.36           | 0.07              | 0.09             | 22.16 |

ethanol as a solvent at 60°C for 3 hours. The synthesized copolymers were reprecipitated several times from ethanol to diethyl ether and dried in vacuum desiccators at 30°C until a constant weight was achieved. The prepared polymers were characterized by FT-IR, <sup>1</sup>H NMR, DSC and mass spectra as well as viscosity. The FT-IR analysis of the prepared polymers was carried out using Perkin Elmer FT-IR. The <sup>1</sup>H NMR spectra of the prepared polymers were carried out using A JEOL EX-270 NMR spectrometer, 270 MHz for <sup>1</sup>H NMR was used with super conducting magnet Oxford and 5 mm Dual probe head for <sup>1</sup>H and <sup>13</sup>C-analysis. Typical conditions are spectral width 4000 Hz for <sup>1</sup>H and 15000 Hz for <sup>13</sup>C; 32 K data points and flip angle of 45°. Particle size and distribution were measured by laser light scattering (Sema Tech, SEM-633, He-Ne laser). The samples were diluted to the required concentration with distilled water before the measurement. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200PC, using aluminum crimped pans under N<sub>2</sub> flow at 20 mL min<sup>-1</sup>. The measurements were carried out between 75°C and +120°C at a heating rate of 10°C min<sup>-1</sup>.

The viscosity of polymer solution was measured at 25±0.1°C using an Ubbelohde viscometer.

**Raw Materials:** The raw materials used in the present study are clinker (C) and raw gypsum (G). Each of those raw materials was separately ground in a steel ball mill until the surface area of 3650 and 2800 cm<sup>2</sup>/g, respectively were achieved. The chemical composition of the raw materials is shown in Table 1. The mineralogical composition of the clinker sample is C<sub>3</sub>S, 58.79%; β-C<sub>2</sub>S, 17.68%; C<sub>3</sub>A, 8.08%; C<sub>4</sub>AF, 9.72%. The Ordinary Portland Cement (M<sub>0</sub>) was prepared by mixing 96 wt.% PCC and 4 wt.% G in a porcelain ball mill for one hour using 3 balls to assure complete homogeneity of the cement. The Blaine surface area [12] of the cement sample was 3350 cm<sup>2</sup>/g.

**Preparation and Methods:** The prepared copolymer (powder) was added to mixing water and then added gradually to 300 g of the dry cement in order to determine the water of consistency and setting time using Vicat apparatus [13, 14]. The determined water was premixed

with the copolymer and was added to 500 g of the dry cement. The resulting cement pastes were directly moulded into one-inch cube stainless steel moulds. The moulds were manually agitated for 2 minutes and then on a vibrator for another 2 minutes to assure the complete removal of air bubbles and voids and to produce suitable pastes. The moulds were kept in a humidity chamber at 100% R. H and a constant room temperature over night, then demoulded and cured in water until the time of testing. Total porosity and compressive strength testing was conducted at 1 day, 3, 7 and 28 days. The compressive strength was carried out using a hydraulic testing machine of Type LPM 600 M1 SEIDNER (Germany) having full capacity of 600 KN [15]. The loading was applied perpendicular to the direction of the upper surface of the cubes. The total porosity, ξ of each sample at any interval was calculated from the following equation [16]:

$$\xi = 0.99 \times W_e \times dp / (1 + W_t)$$

Where 0.99 is the specific volume of the free water, W<sub>e</sub> is the evaporable water content, dp is the bulk density, g/cm<sup>3</sup> and W<sub>t</sub> is the total water content which is equal to the sum of evaporable water (W<sub>e</sub>) and combined water (W<sub>n</sub>) contents. The bulk density (dp) was determined from the following equation:  $dp = W_1 / (W_1 - W_2)$  g/cm<sup>3</sup>, where W<sub>1</sub> is the saturated surface dry weight in air (g) and W<sub>2</sub> is the submerged weight in water (g). To stop the hydration at any age of hydration, a representative sample of about 10 g after the determination of compressive strength was taken, ground in an alumina mortar containing 50 ml of 1:1 (methanol: acetone) solution mixture and then filtered through a sintered glass funnel (G4). The sample was washed with 50 ml fresh diethyl ether, dried at 70°C for one hour and then kept inside an airtight bottle as described elsewhere [16]. The curing water was renewed every week. The combined water content (W<sub>n</sub>) of samples predried at 105°C for 24 hours was determined as the ignition loss at 1000°C for 30 minutes [16]. The workability of OPC pastes was indicated by the slump value of the material measured in a slump test according to ASTM C143.

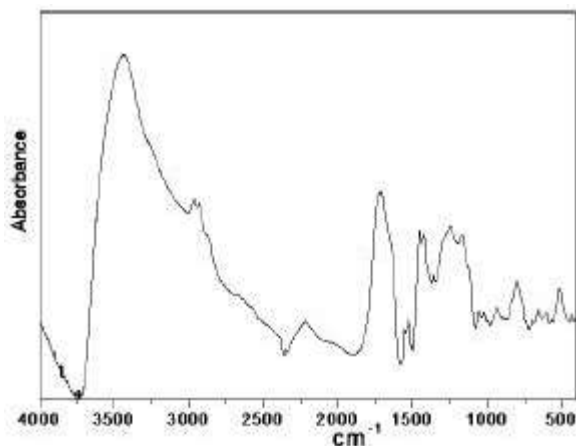


Fig. 1: IR spectrum of water-soluble copolymer

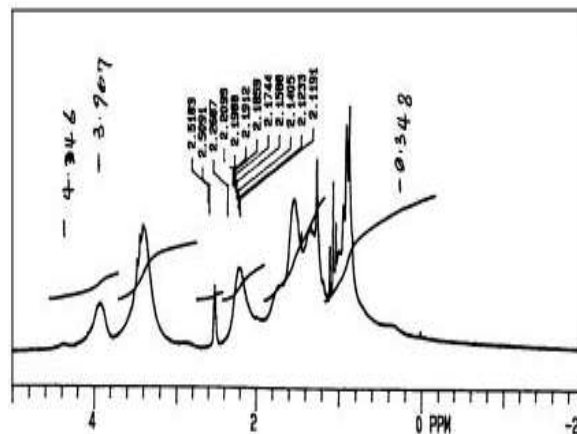


Fig. 2: <sup>1</sup>H NMR spectrum of water-soluble copolymer

Table 2: Chemical shifts of the prepared water-soluble copolymer

| Copolymer          | Resonance Signal (PPM) | Proton                 | Assignment |
|--------------------|------------------------|------------------------|------------|
| Poly[AA-co-BuMA]Na | 1.25-1.53              | -CH <sub>2</sub> - (a) |            |
|                    | 2.11-2.51              | -CH- (b)               |            |
|                    | 4.346                  | -CH <sub>2</sub> - (c) |            |
|                    | 3.37-3.40              | -CH <sub>2</sub> - (d) |            |
|                    | 0.348                  | -CH <sub>3</sub> - (f) |            |

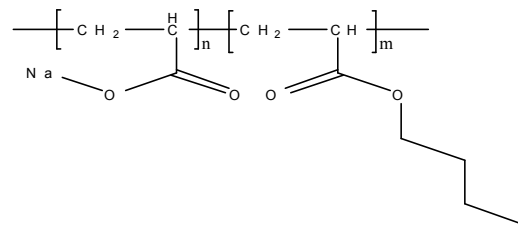
RESULTS AND DISCUSSION

**Characterization of Water-soluble Polymers:** The structure of the prepared water-soluble copolymer [AA-co-BuMA]Na was confirmed by IR, <sup>1</sup>H NMR and mass spectra as shown in Figs. 1 & 2 and Tables 2 & 3 respectively. Fig. 1 shows, the IR spectrum of the copolymer [AA-co-BuMA]Na, where the peak of carboxylate broad band was located at 3442 cm<sup>-1</sup>. The peak at 1712 cm<sup>-1</sup> was due to the C = O stretching band of the carboxylate and ester group. The peak at 1169 cm<sup>-1</sup> occurred because of ether group and the peak at 2962 cm<sup>-1</sup> for CH<sub>2</sub>-aliphatic.

The <sup>1</sup>H NMR spectra gives further support for structure of the copolymers is shown in Fig. 2. The values of the chemical shifts in the characteristic peaks of the copolymer are presented in Table 2.

The characteristic peaks of the mass spectra and values fragment of the main and branched of the prepared copolymer are shown in Table 3. It is clear from the Table 3, that there are characteristic peaks such as number 17 and 95 verified the structure of the prepared copolymer.

The prepared copolymer [AA-co-BuMA]Na is expected to have the structure according to the above characteristics as shown in Scheme 1.



Scheme 1: Structure of Poly [AA-co-BuMA]Na.

Table 4 shows the morphology of the obtained lattices with different compositions such as M1, M2 and M3. It is evident that the values of volume average particle diameter *D<sub>v</sub>* depends on the type of the latex which follows the following order M1<M2 <M3. It has also been reported that polymers with an increase in hydrophilicity facilitate carboxyl ionization, resulting in increase in viscosity, particles with high contents of AA being completely solubilized [17]. Table 4 shows that the particle size decreases and the viscosity increases with increasing amount of AA in the copolymer. The increase in viscosity is mainly due to increase in chain flexibility of the copolymer with the increasing amount of AA. The results also reveal that particle size and viscosity are directly related to the amount of AA and BuMA in the copolymer.

Table 3: Mass spectra of water-soluble copolymer

| No. of peak | Mass | Fragment  |
|-------------|------|---|
| 4           | 53   | $\left[ \text{H}_2\text{C}-\overset{\text{H}}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\overset{\cdot}{\text{C}} \right]$   |
| 14          | 68   | $\left[ \text{H}_2\text{C}-\overset{\text{H}}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\overset{\text{CH}_3}{\text{C}} \right]^{\cdot}$   |
| 17          | 94   | $\left[ \text{H}_2\text{C}-\overset{\cdot}{\text{C}}\text{H} \right]$<br>COONa  |
| 35          | 101  | $\left[ \text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \right]^{\cdot}$  |
| 36          | 120  | $\left[ \text{H}_2\text{C}-\overset{\text{H}}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\overset{\cdot}{\text{C}} \right]$<br>COONa  |
| 58          | 142  | $\left[ \text{H}_2\text{C}-\overset{\text{CH}_3}{\text{C}} \right]^{\cdot}$<br>COOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>   |
| 64          | 155  | $\left[ \text{HC}-\overset{\text{H}_2}{\text{C}}-\overset{\text{CH}_3}{\text{C}} \right]^{\cdot}$<br>COOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>   |
| 71          | 169  | $\left[ \text{H}_2\text{C}-\overset{\text{H}}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\overset{\text{CH}_3}{\text{C}} \right]^{\cdot}$<br>COOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>       |
| 88          | 221  | $\left[ \text{H}_2\text{C}-\overset{\text{H}}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\overset{\cdot}{\text{C}} \right]$<br>COONa COOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>               |
| 95          | 236  | $\left[ \text{H}_2\text{C}-\overset{\text{H}}{\text{C}}-\overset{\text{H}_2}{\text{C}}-\overset{\text{CH}_3}{\text{C}} \right]^{\cdot}$<br>COONa COOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> |

Table 4: Viscosity, Particle size and T<sub>g</sub> of copolymers

| Polymers | η (cps) | D <sub>v</sub> (nm) | T <sub>g</sub> <sup>a</sup> | T <sub>g</sub> <sup>b</sup> |
|----------|---------|---------------------|-----------------------------|-----------------------------|
| M1       | 0.7034  | 80                  | 104.89                      | 105.28                      |
| M2       | 0.6758  | 100                 | 102.69                      | 103.01                      |
| M3       | 0.4528  | 105                 | 100.52                      | 97.24                       |

<sup>a</sup> Predicted using Fox equation

<sup>b</sup> measured using DSC

D<sub>v</sub> is the volume average particle diameter

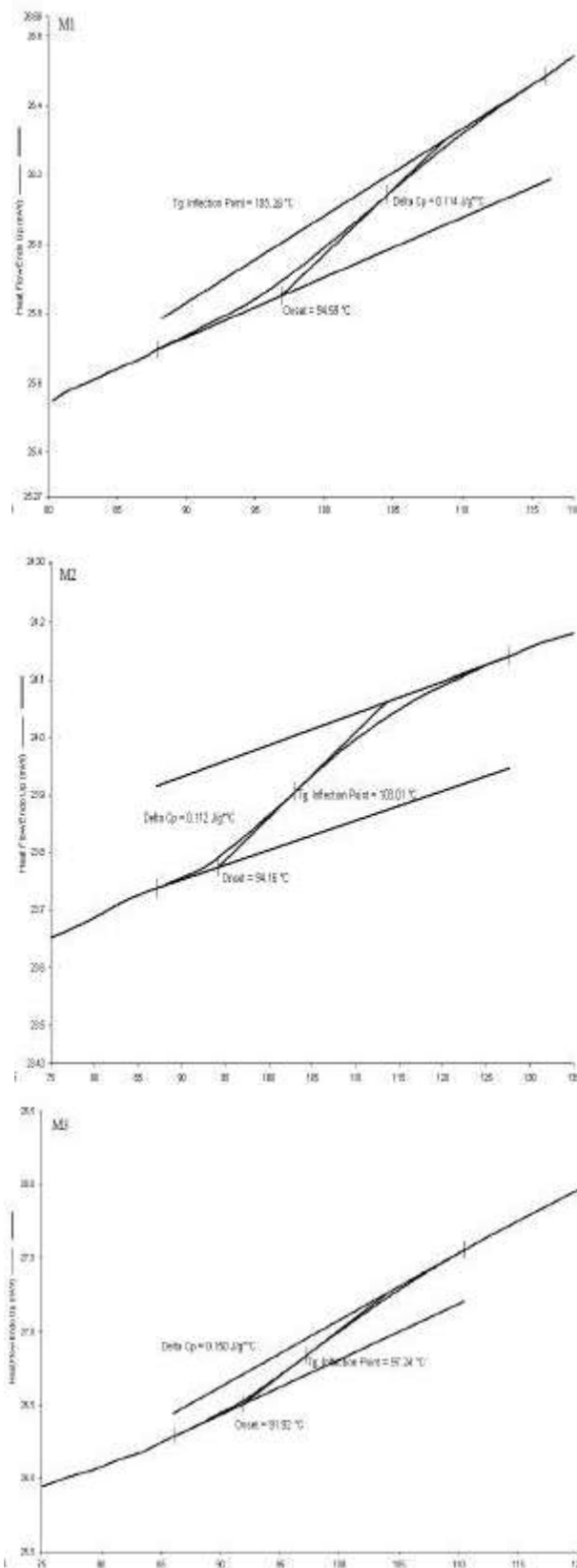


Fig. 3: DSC analysis of Copolymer.

The thermal transitions of the copolymer were determined by DSC analysis and are shown in Fig. 3. The  $T_g$  varies continuously with composition in both AA and BuMA of the copolymer. To describe such type of composition dependence of the  $T_g$  of copolymers, the so-called Fox equation was used [18]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

Where  $T_g$  is the glass transition temperature of the copolymer,  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of the two homopolymers and  $w_1$  and  $w_2$  are the weight fractions of the two repeat units in the copolymer.

The results of DSC analysis of copolymer are summarized in Table 4. As can be seen in Table 4, the experimentally measured  $T_g$  values closely follow the predictions of the Fox equation. Generally, it is known that  $T_g$  is directly proportional to crosslinking density and indirectly proportional to chain flexibility. Results are consistent with this statement. From Fig. 3, it can be seen that the  $T_g$  of copolymer moves toward the lower temperatures as the BuMA increases. The peak located at about 105.28°C is shifted to about 97.24°C as the BuMA increases from 1 to 5% respectively. The decrease of  $T_g$  with increase of BuMA is mainly due to increased plasticity segments in the copolymer structure.

**Application of Water-soluble Copolymer for Cement Water of Consistency and Setting Time:**

Generally, the water/cement (W/C) ratio for the various cement pastes has an important influence on the quality of concrete produced. The cement–water system is highly sensitive to the addition of superplasticizers. Already small amounts of superplasticizers enhance the workability properties efficiently, but are often associated with strong, undesired retardation phenomena of the setting of the cement paste. The results of water consistency as well as setting time of the various OPC pastes mixed with different dosage of water-soluble copolymers are shown in Table 5. It is clear that the W/C ratio of OPC pastes decreases from 28% to 26.8% with addition of the copolymers and then become constant even with increasing the ratios of BuMA in the copolymers. In a general sense, superplasticizers are often used as water reducers, to make concrete stronger by lowering the water/cement ratio [19].

Table 5: Water of consistency as well as setting time of OPC pastes mixed with water-soluble copolymers

| Copolymer | Concentration% | W/C ratio % | Setting time, min. |       |
|-----------|----------------|-------------|--------------------|-------|
|           |                |             | Initial            | Final |
| M0        | --             | 28          | 150                | 360   |
| M1        | 0.25           | 26.8        | 220                | 425   |
|           | 0.50           |             | 275                | 460   |
|           | 1.00           |             | 290                | 560   |
| M2        | 0.25           | 26.8        | 235                | 490   |
|           | 0.50           |             | 285                | 500   |
|           | 1.00           |             | 310                | 575   |
| M3        | 0.25           | 26.8        | 250                | 505   |
|           | 0.50           |             | 305                | 545   |
|           | 1.00           |             | 325                | 595   |

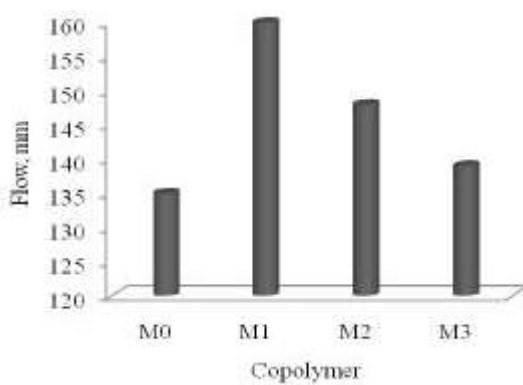


Fig. 4: The effect of the copolymer on the flow of OPC pastes.

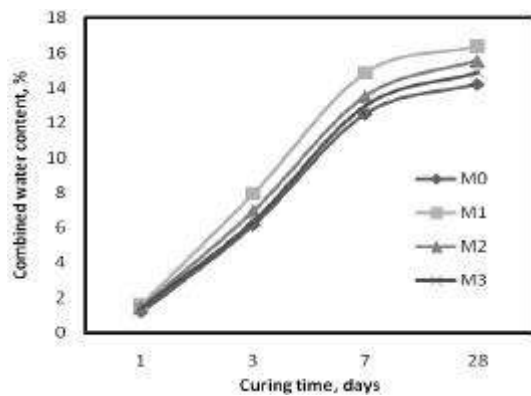


Fig. 5: Combined water contents of the OPC pastes (M0) and those premixed with water-soluble copolymers (M1-M3).

The initial and final setting times of the various pastes are given in Table 5, which shows that as the dosage of the water-soluble copolymer increases, setting times lengthen. This is mainly due to the water loss by evaporation from the outer surfaces of the specimens mixed with the water-soluble copolymers which is relatively less than that of OPC pastes. Furthermore, there

may be a relationship between the type of copolymers and the elasticity of the cement pastes [20, 21]. On the other hand, the setting time of the cement pastes increases with increasing the ratios of BuMA in the prepared copolymers. The delay of setting is thought to relate to the concentration of carboxylate groups in the aqueous phase. The setting time of cement paste depended roughly on the ionic functional group concentration in the aqueous phase of the cement paste [22].

**Workability:** Slump results are presented graphically in Fig. 4. This figure shows that M0 had an initial slump of 135 mm; however there was an increase in slump measurement with the addition of copolymer. OPC paste mix with M1 gave the highest slump with 160 mm while M2 and M3 addition showed a slump measurement of 148 mm and 139 mm respectively. This increase in workability was attributed to the copolymer being a surface active agent.

**Chemically Combined Water Content:** It is estimated that the chemically combined water content is an evidence of the quantitative increase of the newly hydration products that formed in the hardened cement pastes during the hydration process [11, 23]. The combined water contents of the OPC pastes premixed with freshly water-soluble copolymers are graphically plotted as a function of curing time in Fig. 5. The results show that the combined water content of all samples increases with the increase of curing time. It is attributed to that the cement hydration process generally precedes the polymer film formation process by the coalescence of polymer particles in copolymer. It is very important that both cement hydration and polymer film formation proceed well to yield a monolithic matrix phase with a network structure in which the cement hydrate phase and polymer phase interpenetrate. The film forming process in the pore

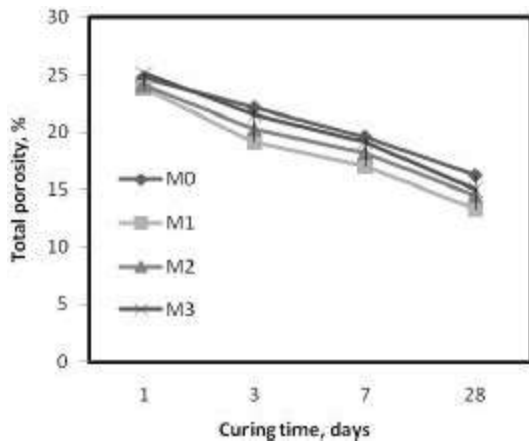


Fig. 6: Total porosity of the OPC paste (M0) and those premixed with water-soluble copolymer (M1-M3).

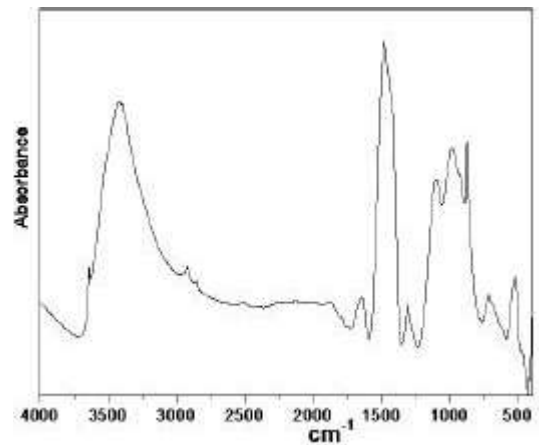


Fig. 8: FT-IR spectrum of OPC mixed with water-soluble copolymers

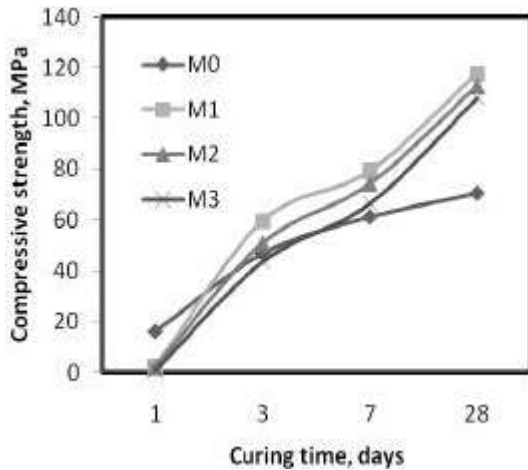
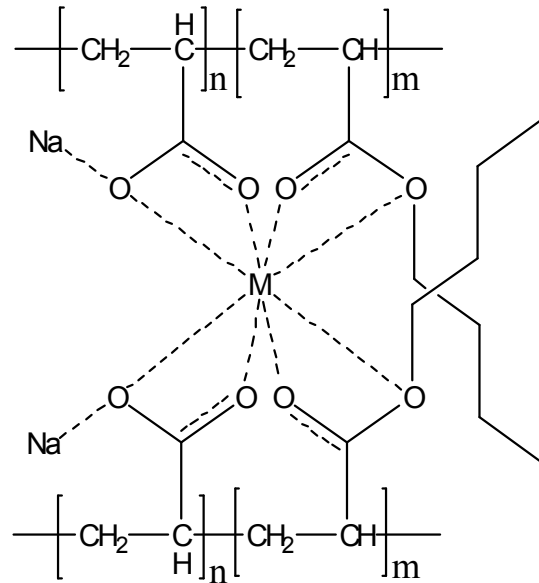


Fig. 7: Compressive strength of the OPC pastes (M0) and those premixed with water-soluble copolymer (M1-M3).



M= Metal

Scheme 2: Complexation of the copolymer with metal of OPC.

solution of cementitious materials can be ascribed to the influence of the altered conditions on the drying rate of the polymer dispersion. In addition, owing to cement hydration, additional forces may be exerted on the water of the polymer particles. Extra water withdrawal results in more closely packed polymer particles and coalescence can take place at even lower temperatures [24].

Furthermore, the combined water content of the cement pastes premixed with the water-soluble copolymers increases with the decreasing in the ratios of BuMA in the copolymers. An admixture having a functional group producing a complex salt, thus decreasing the concentration of  $Ca^{2+}$  in liquid phase at early age and delayings the saturation of  $Ca^{2+}$ , which influences the morphology of hydrate produced [25].

**Total Porosity:** The results of total porosity of the OPC (M0) and the various OPC/copolymer pastes (M1, M2 and M3) are plotted as a function of curing time in Fig. 6. The result shows that, the total porosity decreases with curing time to filling effect of the hydration products. In polymer-modified cement-based material, polymer particles are partitioned between the inside of hydrates and the surface of anhydrous cement grains [26]. The presence of the polymer results in improved pore structure thereby decreased porosity [27].

**Compressive Strength:** The results of the compressive strength of OPC pastes mixed with the prepared water-soluble copolymers with different ratios are represented as a function of curing time in Fig. 7.

The results show that, the compressive strength values of the pastes premixed with the solutions of the water-soluble copolymers are lower than the control paste (M0) during the early ages of hydration up to 3 days then become higher during the latter ages up to 28 days. This is mainly due to the decrease of mixing water, which leads to a decrease of the total porosity and consequently an increase in compressive strength of the cement pastes and this is in good agreement with results reported elsewhere [4, 28, 29]. Furthermore, the compressive strength of the cement pastes premixed with the copolymer solutions increases sharply with the decrease in the ratios of BuMA in the prepared copolymers. Development of high strength of the initial stages is the main application for admixtures of this type [30]. The addition of copolymers does not affect the chemical composition of Portland cement hydration products but only affects the physical state and the degree of crystallinity of the formed hydrates, especially during the early stage of hydration [31]. Hence, there is a considerable influence on the hydration kinetics and the formation of solid structure of cement binder [32]. The results of compressive strength correlate well those of combined water and porosity tests, in that high strength is associated with lower porosity and high amounts of combined water. This is mainly due to that, solutions of sodium acrylate copolymers with a weaker retarding effect led to higher strength than O.P.C pastes without copolymers, however, all superplasticizer improve the plastic and hardening characteristics of the cement pastes leading to higher compressive strength value [33].

FT-IR spectra of O.P.C. mixed with water-soluble copolymers: FT-IR spectrum of O.P.C mixed with the prepared copolymers are shown in Fig. 8. The results show that, the values of stretching frequencies of carbonyl group of the prepared copolymers in the range from (1715-1712  $\text{cm}^{-1}$ ) and for the copolymers mixed with the OPC paste are in range from (1641-1657  $\text{cm}^{-1}$ ). As it is shown that C=O were shifted to lower frequencies due to the complexation [25] between the hydrated cement components and the functional groups present in the hydrophilic polymers as shown in Scheme 2. According to the above facts, the conclusion is that there is stronger force among functional groups of  $-\text{COONa}$ ,  $\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and cement particles.

## CONCLUSIONS

Poly[AA-co-BuMA]Na was prepared and characterized by using FT-IR,  $^1\text{H}$  NMR, mass spectra, DSC as well as viscosity. Mixing the cement pastes with each of the prepared water-soluble copolymers decreased the water of consistency, however, the setting times (initial & final) were prolonged, i.e. the water-soluble copolymers act as a water reducing and set-retarding agents when mixed with the cement. Mixing the cement pastes with the copolymers enhances the combined water contents at all curing ages of hydration. The total porosity of the hardened cement pastes premixed with the copolymers decreases, while the compressive strength increases, especially in presence of 99% ratio of AA in the copolymer. As the ratio of AA in the copolymer increases, the properties of the cement pastes are improved.

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